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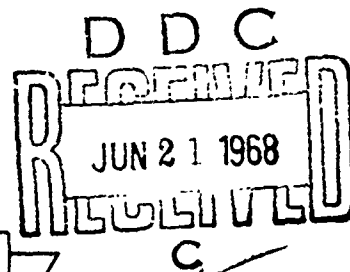
THE PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS DURING
CATHODIC PROTECTION OF STEEL AND IRON IN SEA WATER

by

Chung-tao Tai, Ming-tang Chi and Ching-cheng Koo



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EDITED TRANSLATION

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ABSTRACT: The protective action of white films formed on iron and steel surfaces in sea water under conditions of cathodic protection was studied. Three series of tests were performed with 16 Mn low-alloy steel supplied by the Peking Iron and Steel Institute. In the first series, specimens were exposed either to natural sea water or to 3% NaCl solution, and protected with a constant current. In the second series the specimens were first exposed to stagnant or stirred sea water and for 3 days protected with a high density, $40 \mu\text{a}/\text{cm}^2$, current to form uniform films and then current applied periodically in 24-hr cycles. Specimens of the third series were tested either in natural or artificial sea water with various current densities. The artificial sea water contained either Mg and Ca (pH = 7.7), Mg alone (pH = 7.8), Ca alone (pH = 8.0), or no Mg and Ca (pH = 7.8). Experimental results showed that protection can be achieved in natural sea water at $25 \mu\text{a}/\text{cm}^2$ and in 3% NaCl solution at $35 \mu\text{a}/\text{cm}^2$. Specimens pretreated with a higher current can be protected at $3.5 \mu\text{a}/\text{cm}^2$. The periodically applied current should have a density of $15\text{-}20 \mu\text{a}/\text{cm}^2$. Polarization of Ca-Mg films is 5-8.8 times that of Ca or Mg films, while polarization of Mg films is higher than that of Ca films. Polarization characteristics are affected by current density applied in forming the film. Film formation is more difficult on rusted metal surfaces and more complete in stirred sea water. Films formed at a pH exceeding 10 provide protection for metals; films formed at pH = 9 fail to protect. The authors conclude that calcium-magnesium films have a certain protective ability which makes it possible to use lower current densities in cathodic protection and a shorter period of current application. The dissociation of $\text{Mg}(\text{OH})_2$ in films plays an important role in protection of metals when the current is discontinued. The authors are deeply indebted to Hua Pao-ting of the Applied Chemistry Institute of the Chinese Academy of Sciences for reviewing the

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This paper attempts to study the composition and function of calcium magnesium coatings, their effectiveness, and their effects on the polarization characteristics of steel samples. In addition, studies were also made of the surface structure of the metals, and the effect of the speed of sea water current to the formation of the coatings.

A. RELATIONSHIP OF THE SURFACE STRUCTURE OF STEEL SAMPLES,
COMPOSITION OF THE COATINGS AND CONDITIONS OF THE MEDIA
WITH POLARIZATION AND PROTECTIVE ACTION.

I. Test Procedure

Sixteen Mn low-alloy steel² was used for testing. Samples of three specifications were made according to the requirements of the experiment (see following tables). All separation lines were sealed with acetylene. Surfaces of the samples were polished with diamond sandpapers to such a degree that no scratch marks could be seen with the naked eye.

1. Protection by electric current

Samples used were of rectangular shape (2 x 7 x 0.3 mm), placed separately in 1,000 cc of stable natural sea water and 3% NaCl solution to receive cathodic protection under a constant electric current. The sea water was changed every three days. After the test samples were acid-cleaned and dried, they were weighed. The difference between these weights and the weights before the test was the amount of weight lost. A comparison of the weight lost by protected samples and corresponding samples indicated the degree of protection. The procedure for acid cleaning is as follows: samples were put into an acid cleaning solution composed of 20% HCL and 1% hexa-methyl quaternary ammonium. They were cleaned with a bamboo scraper for three minutes, and then neutralized in 5% Na₂CO₃ solution; rinsed in water, two minutes in 20% NaNO₂ solution, then rinsed in distilled water. The sample was weighed after drying for 24 hours. Corresponding samples went through the same acid cleaning pro-

²See page 18

cedure so any alterations could be noted.

2. Intermittent protection.

Samples were cylindrical in shape (0.46 mm diameter, 7.0 mm long). A cathode current of $40 \mu\text{A}/\text{cm}^2$ was turned on for three days while the sample was immersed in 1,000 cc of stable or stirred-up natural sea water, until a white, even coating of calcium-magnesium appeared over the surface of the sample. Then the sea water was replaced with fresh sea water, and the electric current was reduced, or an intermittent current was used every 24 hours for protection. Otherwise, the acid cleaning procedure and the method used to determine the degree of protection were the same as 1.

3. Study of the effect of the coating on polarization characteristics

Area of sample: 5 cm^2 (double face). Put separately in natural sea water and artificial sea water of different compositions, using electric currents of different intensities (other conditions same as 2), until the calcium-magnesium precipitate coating has formed, then measured cathode polarizations to plot curves. Took readings of electrical potential every 10 minutes when they did not exceed 2 mV. In the secondary polarization curve, when differences in potential values of various reference points did not exceed 10 mV, mean values were taken.

All tests were conducted under a constant temperature of 25°C . Platinum electrodes were used as auxiliary electrodes. Saturated mercury electrodes were used as reference electrodes (all converted to standard hydrogen electrode when plotting diagrams). The potentiometer used was of the UJ type.

Artificial sea water was prepared according to Brujwicz's formula [4]. According to the requirements of the experiments, the calcium-magnesium content was changed as follows:

- a) both calcium and magnesium (pH = 7.7)
- b) magnesium only, no calcium (pH = 7.8)

c) calcium only, no magnesium (pH = 8.0)

d) no calcium, no magnesium (pH = 7.8)

Any other shortage of elements was rectified by proper additions of NaCl. There was no change in other elements.

II. Test Results

From Table 1, we can see that when the intensity of electric current reaches $25 \mu\text{A}/\text{cm}^2$ in natural sea water, complete protection has been achieved. On the other hand, it takes $35 \mu\text{A}/\text{cm}^2$ to achieve the same degree of protection in 3% NaCl solution. The reason is that samples in natural sea water form a calcium-magnesium coating quickly, thereby requiring a smaller amount of protective electric current.

If a stronger current was applied to the surface of the sample to produce a layer of calcium-magnesium coating, the protective current could be reduced, then the intensity of electric current needed to achieve the same degree of protection can be reduced to $3.5 \mu\text{A}/\text{cm}^2$ (Table 2), only one-tenth of the amount required in the 3% NaCl solution. If the electric current was cut off for 24 hours every 24 hours (protection to be provided by the calcium-magnesium coating alone), then the amount of electric current is reduced to $15\text{--}20 \mu\text{A}/\text{cm}^2$. All these results, except the value for the minimum protective current, are close to those in the references [3, 5, 9, 19]. (Reference only listed narrative descriptions without systematic figures.) All these seem to prove calcium-magnesium coatings do possess excellent protective functions.

According to spectral analysis, the main components of precipitation from natural sea water after cathodic protection are calcium and magnesium, plus a small amount of titanium, borax and silicon. To study the effects of calcium and magnesium (the main components) after their precipitation, on the polarization action of steel samples, we prepared artificial sea water to measure the polarization of the precipitations.

The cathode polarization curves of the precipitations from both natural sea water and artificial sea water coincide with each other, except for static potential

TABLE 1. CATHODIC PROTECTION OF 16 Mn STEEL SAMPLE IN SEA WATER, 3% NaCl SOLUTION.

Intensity of protecting $\mu\text{A}/\text{cm}^2$	Medium	Corrosion rate, $\text{gram}/\text{day}\cdot\text{m}^2$	Degree of protection, %	Change in potential (equivalent to standard hydrogen electrode)				Remarks
				12 hours	24 hours	48 hours	72 hours	
0	sea water; 3% NaCl	1.6710	0	-0.5178	-0.5193	-0.5233	-0.5201	yellow rust on surface; serious corrosion on surface.
		3.2470	0	-0.4896	-0.4914	-0.4920	-0.4908	
10	sea water; 3% NaCl	2.2860	29.61	-0.4737	-0.4695	-0.4524	-0.4557	partly corroded.
15	sea water; 3% NaCl	2.2856	82.92	-0.5783	-0.5597	-0.5805	-0.6060	light yellow rust, incomplete thin coating; corrosion concentrated around edges.
		1.7285	46.78	-0.4728	-0.4689	-0.4571	-0.4614	
20	sea water; 3% NaCl	0.0956	94.30	-0.6096	-0.6212	-0.6618	-0.6909	incomplete grayish-white coating and light yellow rust stain on surface; rust on edges.
		1.0730	67.17	-0.4628	-0.4657	-0.4558	-0.4579	
25	sea water; 3% NaCl	0	100	-0.6390	-0.6390	-0.7189	-0.7518	complete grayish-white coating on surface, with white spots; cotton-like rust on edges.
		0.5503	83.13	-0.5999	-0.6262	-0.5715	-0.4721	
30	sea water; 3% NaCl	0	100					gray, hard coating on surface, no corrosion; purplish-black color on surface.
		0.4044	87.56	-0.6377	-0.6319	-0.5350	-0.4712	

TABLE 1. CATHODIC PROTECTION OF 16 Mn STEEL SAMPLE IN SEA WATER, 3% NaCl SOLUTION. (Continued)

Intensity of protecting current $\mu\text{A}/\text{cm}^2$	Medium	Corrosion rate, $\text{gram}/\text{day}\cdot\text{m}^2$	Degree of protection, %	Change in potential (equivalent to standard hydrogen electrode)				Remarks
				+				
				12 hours	24 hours	48 hours	72 hours	
35	sea water;	0.1235	92.63	-0.6903	-0.6882	-0.7340	-0.7646	grayish-white coating on sur- face, no corrosion; lost original luster, dark brown spots appeared.
	3% NaCl	0	100	-0.7496	-0.7262	-0.6893	-0.6863	
40	sea water; 3% NaCl	0	100	-0.7234	-0.7364	-0.7445	-0.7256	bright, no corrosion.

TABLE 2. CATHODIC PROTECTION STATUS AFTER 16 Mn SAMPLES
HAVE ACQUIRED CALCIUM MAGNESIUM COATINGS IN SEA WATER

Method of protection	Intensity of protecting current (ua/cm ²)	Rate of corrosion, gram/24 hours	Degree of protection, %	Change in potential (V) (equivalent to standard hydrogen electrode)								Remarks
				1st day	2nd day	3rd day	4th day	5th day	6th day	7th day	8th day	
Intermittent electric current protection (24 hour cycle)	10.0	0.2904	90.5	electricity off -0.4500	electricity on -0.7593	electricity off -0.4290	electricity on -0.8162	electricity off -0.4525	electricity on -0.8666	electricity off	electricity on	
	15.0	0.675	97.8	-0.4383	-0.8632	-0.5001	-0.9094	-0.5204	-0.8502	-0.5098		no corrosion observed; possible error
	20.0	0.0157	100	-0.5590	-0.8870	-0.4815	-0.9125	-0.5082				
continuous low intensity electric current protection	2.5	1.8504	39.6	1st hr. -0.3909	5th hr.	10th hr. -0.4567	24th hr. -0.4586	48th hr. -0.4670	72nd hr. -0.5023	96th hr. 120th hr.		
	3.5	0	100				-0.6803	-0.7125	-0.7244			
	5.0	0.0701	97.7			-0.6587	-0.7937		-0.7301	-0.8389		no corrosion observed; possible error
corresponding samples	10.0	0.0351	100				-0.6514	-0.7810	-0.8081	-0.8730		no corrosion observed; possible error
	0	3.0670	0				-0.5253	-0.5211				

(Figure 2). But there are appreciable differences between these curves and the polarization curves of single element calcium coatings and magnesium coatings. To reach a standard polarization voltage of 0.6 V, both coatings formed by natural sea water and artificial sea water required $3 \mu\text{A}/\text{cm}^2$, with an average polarization efficiency of $0.2 \text{ V}/\mu\text{A}\cdot\text{cm}^2$; coatings containing only calcium need $26.5 \mu\text{A}/\text{cm}^2$ with an average polarization efficiency of $0.023 \text{ V}/\mu\text{A}\cdot\text{cm}^2$; coatings containing only magnesium need $15 \mu\text{A}/\text{cm}^2$, with an average polarization efficiency of $0.04 \text{ V}/\mu\text{A}\cdot\text{cm}^2$; corresponding blank samples need $30 \mu\text{A}/\text{cm}^2$, with an average polarization efficiency of $0.02 \text{ V}/\mu\text{A}\cdot\text{cm}^2$. The polarization of a combination calcium-magnesium coating is 5 to 8.8 times that of just a calcium or magnesium coating.

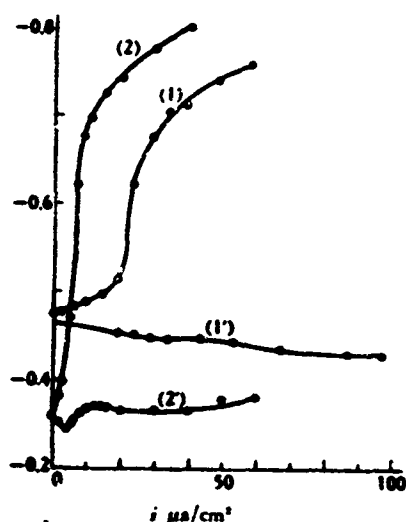


Figure 1. Effects of calcium and magnesium on polarization characteristics. (1) cathode polarization curve of steel samples without calcium-magnesium coating; (1') anode polarization curve of steel samples without calcium-magnesium coating; (2) cathode polarization curve of steel samples with calcium-magnesium coating; (2') anode polarization curve of steel samples with calcium-magnesium coating.

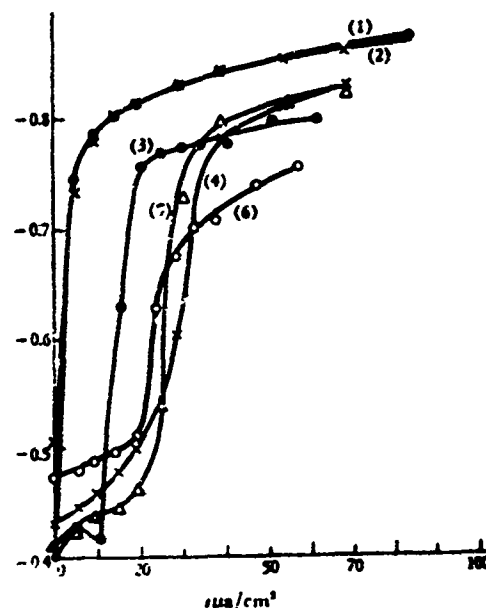


Figure 2. Cathodic polarization curve of 16 Mn steel in different media after formation of coatings (coating formation current $40 \mu\text{A}/\text{cm}^2$; time required, 3 days. Media: (1) natural sea water (●); (2) artificial sea water with both calcium and magnesium (X); (3) artificial sea water with magnesium, no calcium (○); (4) artificial sea water without calcium and magnesium (X); (5) artificial sea water with calcium, no magnesium (Δ); (6) artificial sea water with no coatings (corresponding samples) (○).

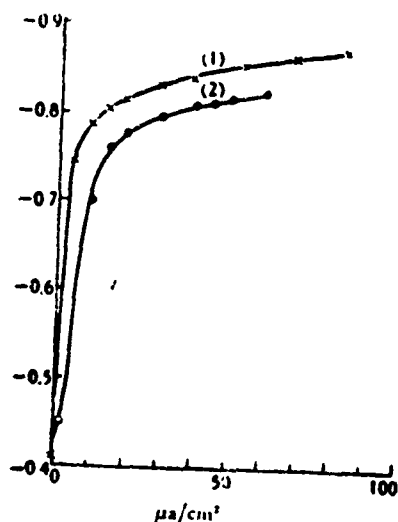


Figure 3. Cathode polarization curve -- after coatings formed using different coating-forming current intensities (medium, natural sea water). (1) coating-forming current intensity, $46.6 \mu\text{A}/\text{cm}^2$ for 3 days; (2) coating-forming current intensity, $40.0 \mu\text{A}/\text{cm}^2$ for 3 days.

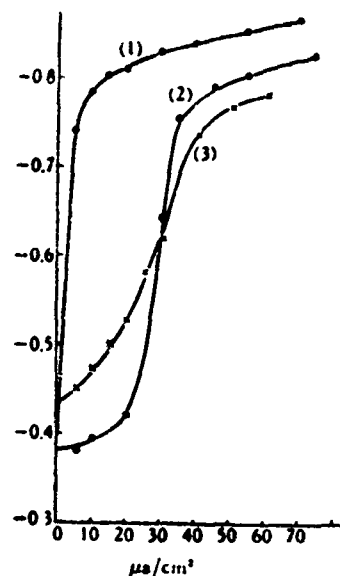


Figure 4. Cathode polarization curve -- after coatings formed under different surface conditions (conditions same as Figure 2; the medium was natural sea water). (1) cathode polarization curve of 16 Mn steel sample after coatings were formed -- bright surface; (2) cathode polarization curve of 16 Mn steel sample after coatings were formed -- surface showing corrosion; (3) cathode polarization curve of 16 Mn steel sample before coatings were formed -- surface showing corrosion.

The electric current intensity during the formation of coatings has a great effect on the polarization characteristics of the coating. A coating-forming current of $46.6 \mu\text{A}/\text{cm}^2$ is apparently higher in polarization characteristics than one of $40 \mu\text{A}/\text{cm}^2$ (Figure 3).

It is more difficult to form coatings (Figure 4) on samples with harder corrosion shells. In stable sea water, the current intensity must be raised to $70 \mu\text{A}/\text{cm}^2$ and above in order to form a relatively complete calcium-magnesium coating.

The stirring conditions of the media also have direct effects on the formation of coatings. If we stabilize the current intensity at $46.6 \mu\text{A}/\text{cm}^2$, and convert the revolving speed of the stirring rod to a linear speed (assuming it is equivalent

to the fluid speed) of 80-90 meters/hour, we noticed a very different situation in the formation of coatings, even better than that which could be achieved in stable sea water. Only a current intensity of $2.5 \mu\text{A}/\text{cm}^2$ was needed to reach a polarization voltage of -0.6 V during polarization, while $3.0 \mu\text{A}/\text{cm}^2$ was needed if the coating was formed in stable sea water. This is due to the fact that slow stirring improves the ionic diffusion requirement of calcium and magnesium. But if the stirring speed increased to the equivalent fluid speed of 470-520 meters/hour, then the same current intensity could not form a good coating, and the sample corroded quickly. This is because the pH value of the medium could not be quickly raised due to stirring, and in the meantime, depolarization due to oxygen was speeded up. But if the current was raised to $70 \mu\text{A}/\text{cm}^2$ and above, we could see the formation of good coatings again.

B. OH^- PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS.

I. Test Procedure

Sixteen Mn cylindrically shaped samples (0.46 cm diameter, 7.0 cm long), were used. Direct current was introduced while sample was immersed in natural sea water (or artificial sea water (1 liter) at $40 \mu\text{A}/\text{cm}^2$ for 3 days, under a constant temperature of 25°C , until a white, even calcium-magnesium coating (thickness 0.1-0.3 mm) was formed. A scalpel was used to carve out small holes (diameter, 0.5-2 mm) along the axis line and spaced 1 cm apart, so that the basic metal was exposed. The sample was then immersed in fresh sea water, to observe its corrosion status.

The sample was gently flushed with distilled water, its calcium-magnesium coating removed (coatings from the corroded and noncorroded areas in the same sample were taken separately to conduct separate tests), 5-10 cc distilled water was added, and the coating was repeatedly stirred. After half an hour the pH value of the upper part of the clear solution was tested.

TABLE 4. POTENTIAL DIFFERENCE BETWEEN COATINGS ON STEEL
SAMPLE SURFACES AND THE SMALL HOLES

Type of Coating	Potential (Equivalent to Standard Hydrogen Electrode)	
	At Small Hole Area	Coating Area
Calcium-magnesium coating	(1) -0.478	-0.479
	(2) 0.487	-0.488
Clear Lacquer	-0.435	-0.436

II. Test Results

In the experiment concerned with drilling holes through calcium-magnesium coatings on the sample surface, 8 tests were conducted and 40 holes were tested. Of these, only 3 revealed blue or yellow corrosion stains within 8 hours. The other part of the sample did not reveal any corrosion stains within this period of time. Furthermore, when stretched into longer periods, corrosion only developed at the original places. Other areas retained their bright metallic sheen. On the other hand, corresponding samples with three coats of clear varnish, from ten tests of 50 holes, revealed yellow or blue corrosion stains in 47 holes within 5 hours. In addition, when calcium-magnesium coatings were peeled off in patches to the point where their areas were one-third of the total area of the sample, corrosion stains began to occur within 2.5 hours. Therefore, it is not enough to explain this phenomenon from the viewpoint of physical shielding. The theory regarding the protective aftereffect of the coatings is also rather hazy, since it does not explain the real reason for the protective aftereffect.

Calcium-magnesium coatings, in addition to their mechanical shielding action, also exhibit other types of protective action.

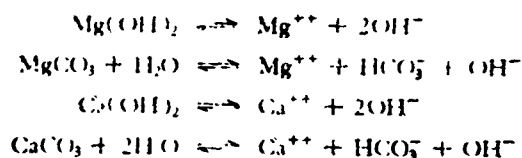
Because sea water possesses good electrical conductivity, there are no appreciable differences between the voltages of the coating area and the small hole

TABLE 5. RELATIONSHIP BETWEEN THE PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS AND pH.

Medium in which coating was formed	Where samples were taken from	pH Value	Corrosion at small hole areas	Remarks
natural sea water	sea water before test; sea water after test; solution formed by coating.	8.19 8.13 10.20	in 8 tests, within 8 hours, only 3 out of 40 holes showed yellow rust. Others preserved their bright metal sheen.	coating samples taken and analyzed right after current cut off.
artificial sea water (contains both calcium and magnesium)	sea water before test; sea water after test; solution formed by coating without corrosion; solution formed by coating with corrosion.	8.08 — 10.12 9.31	in 1 test, within 8 hours, none of the 5 holes showed blue or yellow rust. All preserved bright metal sheen.	coating samples analyzed after soaking in natural sea water for 4 days after current cut off.
artificial sea water (contains only magnesium)	sea water before test; sea water after test; solution formed by coating without corrosion; solution formed by coating with corrosion.	8.24 — 10.12 9.16	in 4 tests, within 5 hours, 7 out of 20 holes showed yellow rust. Others preserved bright metal sheen.	coating samples analyzed after soaking in sea water (natural) for 5 days after current cut off.
artificial sea water (contains only calcium).	sea water before test; sea water after test; solution formed by coating.	7.60 7.53 9.12	within 5 hours, large area (more than 1/3) showed yellow rust. Coating provided no protective action.	coating samples analyzed after soaking in natural sea water for 2 days after current cut off.
distilled water	corresponding tests	6.90		

structure (gaps in structure mutually filled up), and thereby greatly increases polarization efficiency.

2. We feel, however, that during the time of electricity cut-off, such calcium-magnesium coatings possess OH^- protective action, in addition to their mechanical protective-coating function. This kind of coating is porous, therefore, due to the gradual decomposition of its hydroxides and carbonate salts; a solution of higher pH fills these small pores.



Therefore, even after the electricity cut-off, such coatings, due to their own dissolution, can still release a certain amount of base, which affects the solution in the pores and the thin layer of relatively stable solution on the surface of the sample (approaching the pH value when the coating reaches decomposition equilibrium), or can even form a new thin layer of precipitation around the small holes (we observed that during the experiment it could be formed by calcium carbonate) to protect the metal within the small holes.

The self-dissolution of the coating begins with the hydroxides of the magnesium. At this time the pH value of the surface of the sample is always maintained above 10 (shortly after the electricity cut-off, pH value should be higher than the time of decomposition equilibrium due to the existence of excessive OH^-), which provides protective action to iron and steel. When the hydroxides of the magnesium in all of the local areas begin to dissolve, the calcium salts begin to dissolve. pH value by this time drops to about 9.1, losing its protective action to iron and steel, and corrosion in spots and larger areas begins to appear.

3. Krasnoyarskiy maintains that a calcium-magnesium coating exhibits a protec-

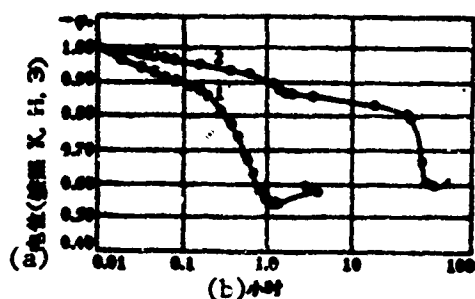


Figure 5. Time versus voltage curve, when electricity was cut off after steel sample was polarized for 48 hours under an electric current of $25 \mu\text{A}/\text{cm}^2$. (1) 30 g/liter of NaCl; (2) 3.74 g/liter of MgSO_4 , 2.76 g/liter MgCl_2 , and 1.5 g/liter CaCl_2 [according to Krasnoyarskiy]. Key: (a) potential (according to K, H, E); (b) hours.

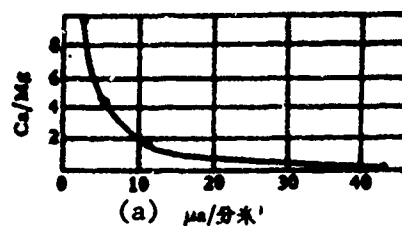


Figure 6. Change in the relative ratio of calcium and magnesium in the coating with the change of electric intensity [according to Krasnoyarskiy]. Key: (a) $\mu\text{A}/\text{cm}^2$.

tive aftereffect, but this does not explain why a "protective aftereffect" still exists in NaCl solution without the formation of a calcium-magnesium coating (Figure 5) [7]. We feel this is due to the effect of electricity. A highly concentrated OH^- layer is produced around the electrode, which makes it possible to maintain protective action for a definite period even after the electricity cut-off when no calcium-magnesium coating has been formed.

In the meantime, we feel that Krasnoyarskiy's theory that cathode polarization causes the protective aftereffect of a calcium-magnesium coating only explains the superficial phenomenon. A fuller explanation should be: since a calcium-magnesium coating contains a larger concentration of OH^- (excess and decomposed), it causes the metal to maintain a higher negative voltage. The concentration of OH^- begins to diminish with the passage of time, while in the meantime oxygen has permeated through the coating to reach the metal surface. Both factors cause the change in voltage, and eventually the sample loses its protective action.

4. For practical purposes, we hope the magnesium content of the coating can be increased. The ratio of calcium compounds to magnesium compounds depends on the

intensity of the electric current. When we raise the current intensity, the relative quantity of magnesium compounds can be raised (Figure 6) [7].

D. CONCLUSION

The calcium-magnesium coating formed on the surface of iron and steel during cathodic protection in sea water posses distinct protective functions, which can save 9/10 of the protective electric current and half of the time required for protection. A calcium-magnesium coating is more densely constructed than simply a calcium or magnesium coating, therefore it has a higher polarization efficiency. A magnesium coating has a higher polarization efficiency than a calcium coating.

Many authors abroad maintain that this kind of coating only produces a mechanical protective-coating action. The authors of this paper feel that such a theory is not complete. The correct explanation should be as follows: when the electric current is on, it essentially produces a mechanical protective-coating action. When the electric current is turned off, it still maintains protective action provided by OH^- . When the pH value of the coating is maintained above 10 (equivalent to the decomposition equilibrium pH value for $\text{Mg}(\text{OH})_2$), the voltage is maintained at the proper negative value, causing no corrosion of the iron. When the pH value of the coating drops below 9 (equivalent to decomposition equilibrium pH value of $\text{Ca}(\text{OH})_2$), the voltage readings become positive, which causes corrosion to appear. The OH^- protective action of the coating is provided by the decomposition of $\text{Mg}(\text{OH})_2$. Calcium coating does not have protective action.

The surface condition of the metal, current speed of the sea water and the intensity of the electric current also have strong effects on the precipitation of the coating and its protective action.

Footnotes

1. to p. 1. Research report No. 113, Oceanographic Research Institute, Academia Sinica. This paper was presented to the Third National Corrosion Prevention and Protection Conference in 1964. Amendments and revisions were made after the conference. Acknowledgement and appreciation are given here to: Mr. Pao-ting Hua, Applied Chemistry Research Institute, Academia Sinica, for proof-reading and offering many valuable suggestions for revision; Mr. Ming-hou Chi of this Institute for his great encouragement and assistance; Mr. Shou-an Fan for participating in part of the experimental work.
2. to p. 2. Acknowledgement and thanks are given here to the Iron and Steel Research Institute of Peking for supplying the samples.

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